Structure and Energetics of Electrodeposited AgI

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The initial stage of underpotential deposition of silver on an iodine-covered Pt(111)($\sqrt{7}$ x $\sqrt{7}$)R19.1°-I surface gives a (3 x 3) structure with Ag and I coverages of 4/9 ML. We have previously analyzed this surface using quantitative LEED measurements in the tensor-LEED approach [1]. The surface is found to be like a two-layer (111) slice of bulk AgI in the zinc-blende form as originally suggested by Hubbard [2], though the registry of the Ag atoms with the Pt substrate is different. The Ag and I layers have no significant corrugations; one of the Ag atoms is in a 3-fold fcc site on the Pt substrate and the other three Ag atoms in the unit cell are on "near atop" sites on the Pt.

We sought to supplement this structural data with energetic data in order to gain insights into the nature of the bonding in the AgI surface compound. In particular, we combined a variety of surface science and electrochemical measurements in order to determine the cohesive energy of this compound. Below we denote the ($\sqrt{7}$ x $\sqrt{7}$)-I structure by I(ads) and the (3 x 3)-AgI structure by I(ads). Since the ordered phases interconvert directly by an island growth mechanism [3], we take the standard state as the fully-covered ordered phase. The temperature dependence of the potential of the deposition peak in voltammograms was used previously [4] to determine that the entropy of reaction (1) below is -30 J K^{-1} mol^{-1}. The peak position gives the Gibb's energy as 44 kJ mol^{-1}, and combination of the Gibb's energy with the entropy gives the enthalpy change as +36 kJ/mol.

The enthalpy change on emersing the adsorbed iodine layer from the electrolyte into vacuum (reaction 2) was estimated from the measured contact angle of 55°. The enthalpy change for desorption of iodine atoms into the vacuum (reaction 3) was estimated from an analysis of thermal desorption spectra, in the framework of a transition-state model making mean-field assumptions about the configurational entropy of the adsorbed layer. Estimates were also make for the contribution of lattice vibrations and the repulsions between adsorbed iodine atoms. Combination of the data for the three reactions was combined with literature data for the vaporization of silver (reaction 4) to give the cohesive enthalpy of the AgI(ads) structure:

(1) AgI(ads) → I(ads,aq) + Ag(s)	ΔH^o = +36 kJ/mol
(2) I(ads,aq) → I(ads,vac)	ΔH^o = +7 kJ/mol
(3) I(ads,vac)→ I(g)	ΔH^o = +209 kJ/mol
(4) Ag(s) → Ag(g)	ΔH^o = +285 kJ/mol
(5) AgI(ads) → Ag(g) + I(g)	ΔH^o = +537 kJ/mol

The significance of the calculated cohesive enthalpy in the context of some simple models of bonding will be discussed.

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